



Low Temperature Synthesis and Characterization of rGO-CoO Nanocomposite with Efficient Electrochemical Properties

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Abstract

Graphene has been offered as a promising two dimensional nanomaterial with outstanding electric, thermal and mechanical properties for many applications. Here we narrate a facile approach to prepare a reduced graphene oxide-cobalt oxide nanocomposite (rGO-CoO) via a general co-precipitation method at 80 °C and within 6 hours reaction period and the final product was annealed at 500 °C. Transmission electron microscope images show that the cobalt oxide nanoparticles (10-20 nm) are encapsulated by a reduced graphene oxide shell. The oxidation states of the nanocomposite were confirmed by XPS studies. The electrochemical properties of the nanocomposite were investigated by using cyclic voltammetry (CV). A maximum specific capacitance of 175 F/g was obtained at a scan rate of 10 mV/s.

Keywords: Cobalt oxide; Electrochemical properties; Graphene oxide; Nanocomposite; Structural properties.

1. INTRODUCTION

In recent years, Graphene has concerned tremendous attention for its outstanding electronic and thermal conductivity, high surface area (2630 m²/g) (Zheng *et al.* 2014), high mobility of charge carriers, very good chemical stability and mechanical strength due to its unique structure (Han Hu *et al.* 2012). In addition to these properties, graphene has many potential applications in super capacitors (Wood *et al.* 2014), electrochemical energy storage devices (Wu *et al.* 2012), biosensors (Jiang *et al.* 2012), enzyme free glucose detection (Dong *et al.* 2012), low cost water purification treatments (Wei Gao *et al.* 2011), flexible conductors (Lee *et al.* 2012) and Li-ion battery electrodes (Jixin Zhu *et al.* 2011). Though the graphene science is yet young, owing to the future perspectives and an application of graphene is very lustrous (Chenlu Bao *et al.* 2012), this subject area requires lots of fresh and ground breaker works.

Literature survey (Sukeun Park *et al.* 2012) has revealed that, electrochemically active materials like, Sn, Si and metal oxide like, Co₃O₄, RuO₂, IrO₂, MnO₂ and NiO_x have been effectively considered as materials for super capacitors. Cobalt oxide (Co₃O₄)

has been reported to be high performance electrode material for super capacitors, due to its relatively low cost, high redox activity, great reversibility and its high theoretical specific capacitance (~3560 Fg⁻¹). Owing to these characteristics, (Co₃O₄) / GNS has been considered a precursor for electrochemical super capacitors (Jun Yan *et al.* 2010).

In this work, we present a co-precipitation approach to prepare the nanosized CoO nanoparticles decorated with graphene oxide nanocomposite and evaluate their electrochemical performance. The synthesis method is fast and effective to disperse particles on GO sheets. It is expected that CoO nanoparticles decorated with graphene oxide nanocomposite could exhibit high specific capacitance and excellent cycle ability.

2. EXPERIMENTAL

2.1 Preparation of Graphene Oxide

Graphene oxide was prepared according to the modified Hummer's method that has been reported previously (Xu *et al.* 2012; Hummers *et al.* 1958) and

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utilizes graphite powder from sigma Aldrich (SP-1 grade 325 mesh). In a typical synthesis, graphite powder (10g) was added into an 80 °C solution of concentrated H₂SO₄ (20 mL), K₂S₂O₈ (4.2 g), and P₂O₅ (4.2 g) and the dark blue mixture was stirred vigorously and kept at 80 °C for 4.5 h. That mixture was cooled to room temperature, and diluted with 45 mL of deionized water. Finally the solution was transferred to a large beaker, and left overnight. The mixture was then carefully filtered and washed with deionized water using 0.22 µm polycarbonate filter until the pH value was reached to neutral. The obtained product was dried at 40 °C for 24 hours under vacuum.

The pre-oxidized graphite powder was then allowed to oxidation by Hummer's method. 2 g of pre-oxidized graphite powder was added into 46 mL of concentrated H₂SO₄ at cold (0 °C) condition. Then 12 g of KMnO₄ was added gradually under stirring and prevent the temperature of the mixture not exceeding 20 °C. Then, remove the ice-bath and the mixture was stirred at 35 °C for 2 hours. After, 97 mL of deionized water was slowly added gradually into the mixture and the diluted suspension was maintained at 98 °C for 15 min. Again, added 280 mL of deionized water and 5 mL of 30% hydrogen peroxide were added into the suspension turned bright yellow. The brilliant yellow mixture was obtained and the product was centrifuged and washed with 10% HCl aqueous solution to remove the excessive residual metal ions followed by deionized water to remove the acid until the pH of filtrate was neutral. The final solid product was dried in vacuum at 40 °C. Exfoliation was done by sonicating the oxidized graphite dispersion for 30 min at 240 W. The prepared Graphene Oxide was dried in vacuum at 40 °C for 24 h.

2.2 Preparation of Reduced Graphene Oxide – Cobalt Oxide Nanocomposite

Preparation of reduced graphene oxide – cobalt oxide nanocomposite, Graphite oxide was added an aqueous solution 0.1 M Cobalt acetate hexahydrate and the solution was sonicated and 0.6 M of NaBH₄ was gradually added drop wise to the above solutions. Then it was stirred for 30 min at room temperature. Subsequently the solution was vigorously stirred for 6 h at 80 °C. The solid product was collected by centrifugation and washed several times with deionized water and absolute ethanol, respectively. The final product was dried in a vacuum oven at 60 °C for 12 h. The obtained final product was annealed at 500 °C for 5 hours and used for the characterizations.

2.3 Materials Characterization

The synthesized rGO-CoO nanocomposite samples were subjected to XRD analysis. The XRD pattern was recorded (model: X'PERT PRO PAN analytical) using Cu K α radiation ($\lambda=1.54060$ Å) with nickel monochromator in the range of 2θ from 10° to 80°. The XPS measurements were performed with XPS instrument (Carl Zeiss) equipment. The spectra were at a pressure using ultra high vacuum with Al K α excitation at 250 W. The morphology of the synthesized rGO-CoO nanocomposite was examined using SEM and TEM. The morphology of the final product was characterized by Field emission scanning electron microscopy (ZEISS EVO MA 15). The elemental composition of the as-prepared samples was quantified by energy dispersive spectroscopy (EDS) using an X-ray detector (THERMO EDS) attached to the FESEM instrument. Samples for TEM (model: Tecnai F20) analysis were prepared by drop coating the nanoparticle solutions on carbon-coated copper grids at room temperature. The excess nanoparticle solution was removed with filter paper. The copper grid was finally dried at room temperature and was subjected to TEM analysis by the instrument Tecnai F20 model operated at an accelerating voltage of 200 kV. Moreover, Fourier transform infra-red spectroscopy (FT-IR) analysis was carried out in the range of 400-4000 cm⁻¹ (Perkin Elemer). The Micro Raman analysis of our samples was carried out using the instrument of Princeton Acton SP2500, CS spectrometer 0.5 Focal length triple grating monochromotor excitation source Ar⁺ laser.

2.4 Electrochemical Investigation

All electrochemical measurements were performed on a CHI 660 °C electrochemical workstation in 1 M aqueous KOH electrolyte using a three electrode system. Platinum wire and Calomel electrode were used as the counter and reference electrodes, respectively. The working electrodes were fabricated by using available literature (Chen *et al.* 2009). 80 weight % of prepared powders (rGO-CoO) was mixed with 15 weight % of acetylene black and 5 weight % of polytetrafluorene– ethylene (PTFE) binder. A small amount of ethanol was added to the mixture to produce a homogeneous paste, which was pressed onto graphite sheet current collectors (1 cm X 1 cm) to make electrode. Before the electrochemical test, the prepared electrode was soaked overnight in a 1 M KOH solution.

3. RESULTS & DISCUSSION

X-ray diffraction measurements have been recorded during different steps of preparation of nanocomposites. Figure 1a depicts the XRD studies of the GO materials, which is due to the oxidation process of graphite. The effective oxidation of graphite and the formation of GO has been compared with the characteristic strong and sharp (002) peak at 11.02° (Elzatahry *et al.* 2012; Gao *et al.* 2013).

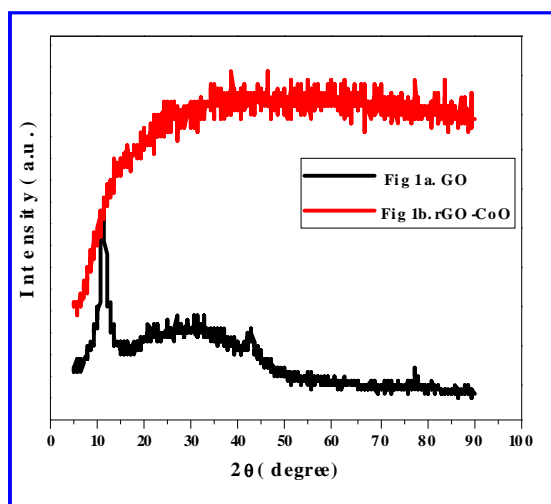


Fig. 1: XRD Pattern of GO and RGO-CoO Nanocomposite

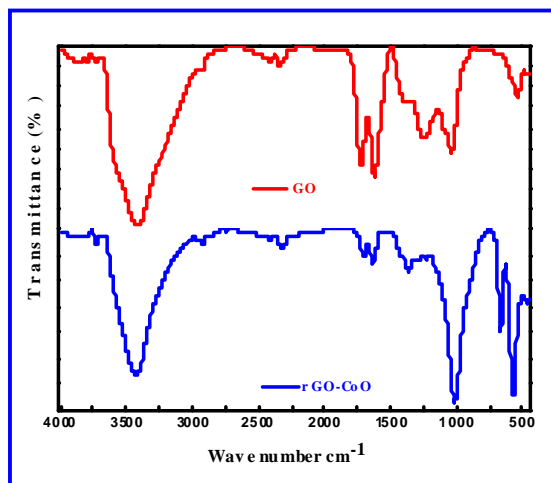


Fig. 2: FTIR Spectra of GO and rGO-CoO Nanocomposite

In another hand figure 1b shows the X-ray diffraction pattern of the rGO-CoO nanocomposite. As seen from the figure, there were no prominent peaks. Which demonstrated that the rGO composite

prepared via a hydrothermal method was amorphous. Since there are no characteristic diffraction peaks of Co metal at $2\theta = 44.2^\circ$, 51.5° and 75.9° , we can assume the presence of Co in the form of its oxide, CoO (Zhang *et al.* 2013). As compared to the graphene, CoO dominated and hence the graphitic peak was absent. In the XRD pattern, there is a slightly broadened but not well defined peak at 25° . These results could be attributed to the relatively short domain order arrangement of graphene stacked sheets. The characteristic peak of graphitic carbon was weak representing that the carbon structures in graphene oxide are disordered (Lian *et al.* 2010). The sodium borohydrate reduction, the Cobalt oxide was not fully reduced to Co nanoparticles. It was present in the form of CoO. From the XPS data it was confirmed.

Fig. 2a and 2b show the FTIR spectra of graphene oxide and rGO-CoO nanocomposite. The IR frequencies at 3411 cm^{-1} , 1725 cm^{-1} , 1038 cm^{-1} and 1237 cm^{-1} confirms the presence of many oxygen containing groups such as OH, C=O, C-O, C-OH respectively in graphene oxide. These evidences indicate that during the oxidation process of the graphite powder with KMnO_4 in the concentrated sulphuric acid, the original extended conjugated π -orbital system of the graphite were destroyed and oxygen-containing functional groups were introduced into carbon skeleton (Lian *et al.* 2010). When compare with the FTIR spectra of rGO-CoO nanoparticles, the weak band at 571 cm^{-1} corresponds to stretching vibrations of $\text{Co}^{2+} - \text{O}^{2-}$ (Wang *et al.* 2013).

To determine the chemical composition of rGO-CoO nanocomposite, X-ray photoelectron spectroscopy (XPS) measurements were carried out. The Co 2p XPS spectra (Fig. 3a) of the composite display two peaks at 795.8 eV and 780.49 eV, consistent to the Co $2p_{1/2}$ and Co $2p_{3/2}$ spin orbital peaks of Co in fig. 3b. It is confirming the CoO species in the hybrids (Zhang *et al.* 2013; Wang *et al.* 2013).

In addition figure 3c shows the high resolution C 1s XPS spectra of rGO-CoO nanocomposite and GO respectively. The binding energy of 284.1 eV is consigned to the C-C and C=C bonds, whereas the binding energies above 286.5 eV can be ascribed to the oxygen functional groups, such as C-OH, C=O and O=C-OH. As shown in figure 3c the intensity of oxygenated functional groups on carbon sheets in nanocomposite is obviously reduced as compared to that of graphene oxide which point out that the graphene oxide has been reduced during the formation of nanocomposite (Yao *et al.* 2013). Moreover the oxygen (O 1s, 531.8 eV) signals from

graphene sheets in fig. 3d, and the O 1s peak witnessed at 530 eV is consigned to the oxygen bonded with cobalt (Fan *et al.* 2013).

A typical SEM image of the GO is given in fig. 4a and 4b which shows a simple nanosheet morphological structure (Ashok Kumar *et al.* 2012). The SEM image of the as-prepared nanocomposite and their calcinated products are presented in figure 4c and 4d. Wave like surface morphology nanosheets is observed for the entire reconstructed nanocomposites.

Further, more it is clearly seen from TEM images of these samples (Fig. 5a-d) that even after strong sonication, most of these CoO particles still remains on the surface of the graphene oxide layers, indicating a relatively strong interaction between CoO and graphene oxide. Figure 5a and 5b shows the low magnification TEM images of rGO-CoO sample and Fig 5c and 5d shows the high magnification of the rGO-CoO sample. From the TEM images rod like structure of rGO-CoO nanocomposite was obtained.

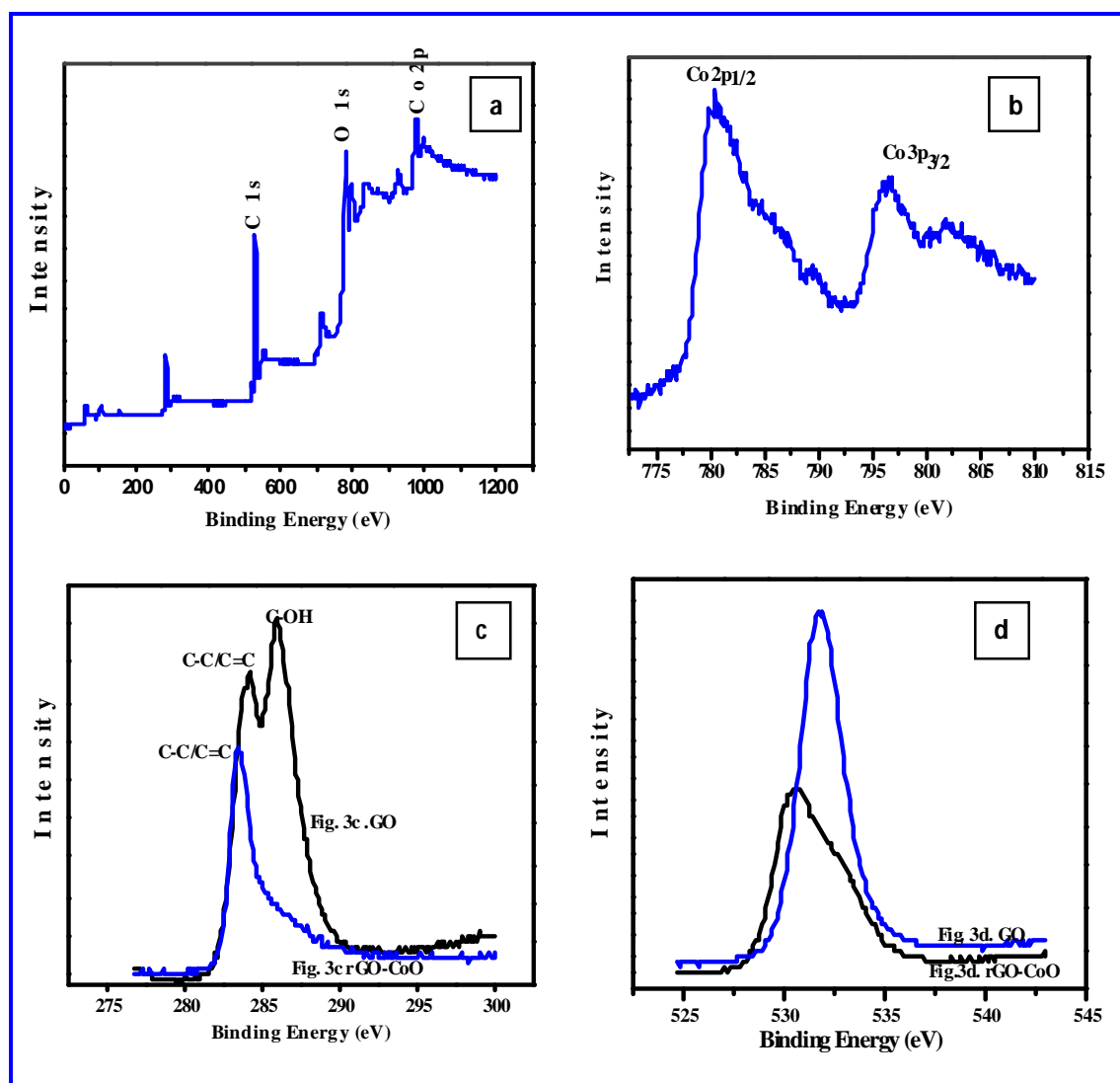


Fig. 3: a) XPS spectrum of rGO-CoO nanocomposite b) XPS spectrum of Co 2p c) XPS spectra of GO and rGO-CoO d) O-1s XPS spectrum of GO and rGO-CoO

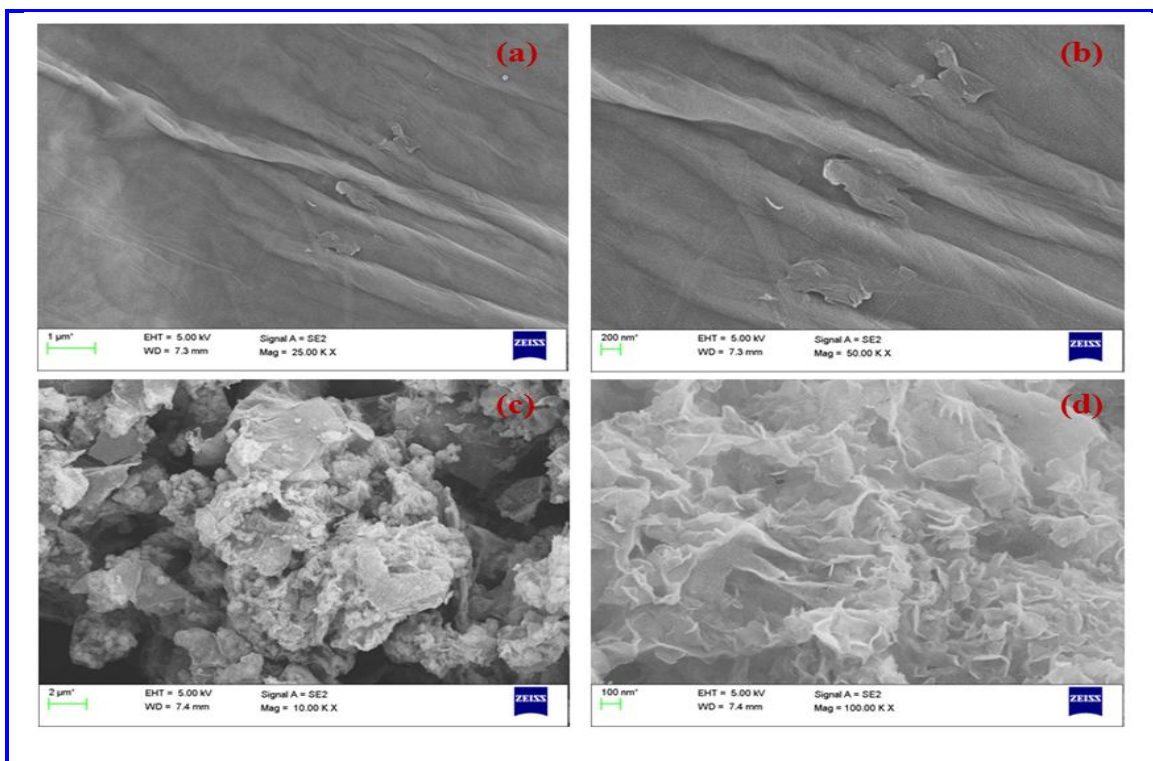


Fig. 4: (a & b) Low and High magnification SEM images of GO. (c& d) Low and High Magnification SEM images of rGO-CoOnanocomposite

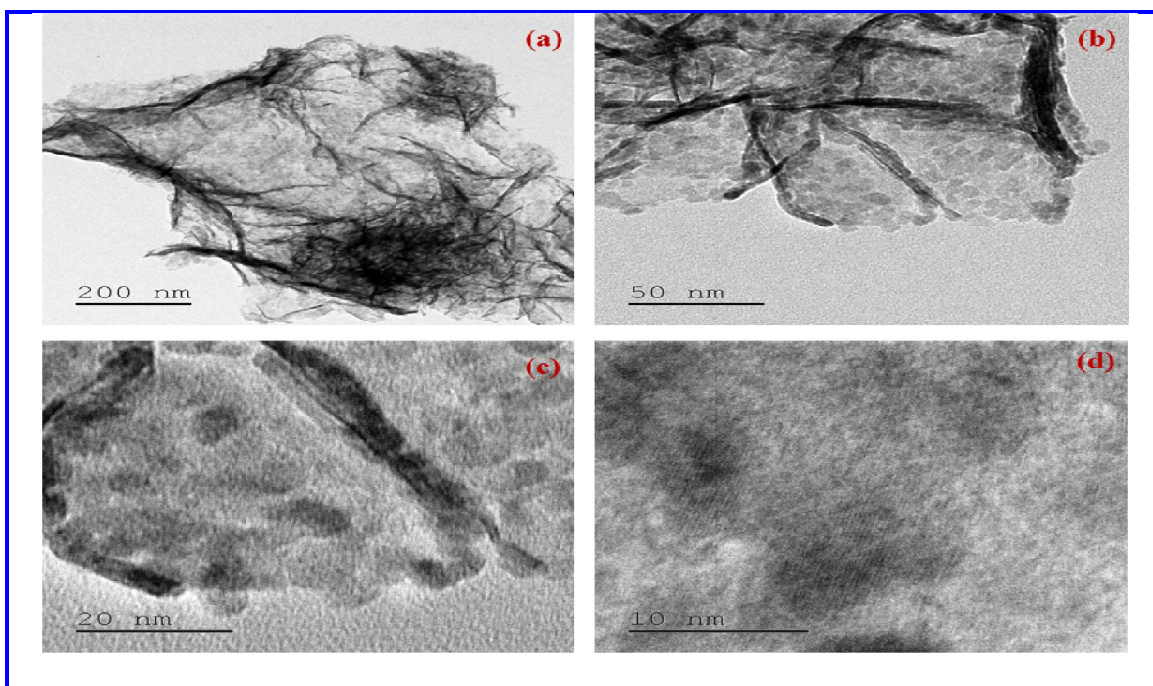


Fig. 5: (a-d) Low and High magnification TEM images of rGO-CoOnanocomposite

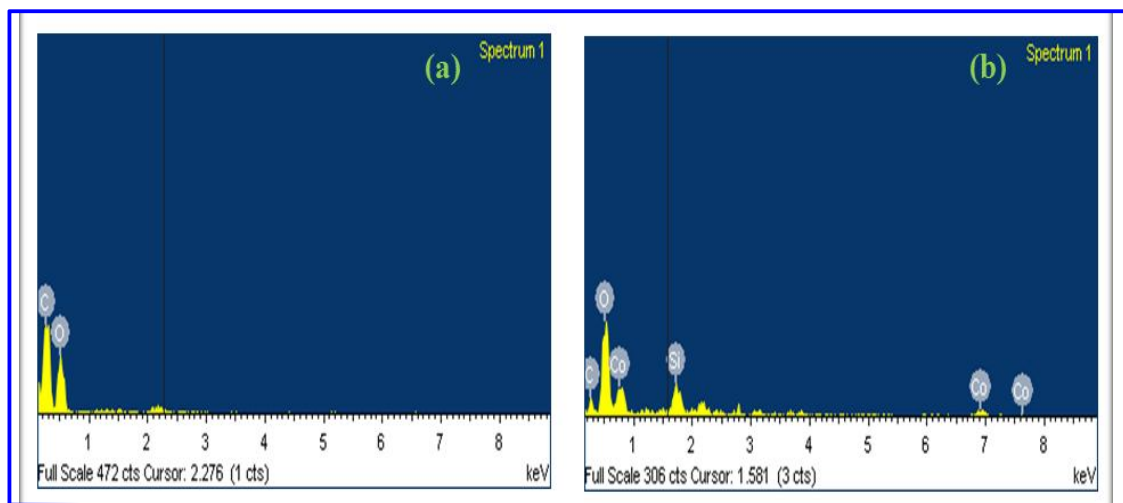


Fig. 6: (a)EDS analysis of GO. (b) EDS analysis of rGO-CoO

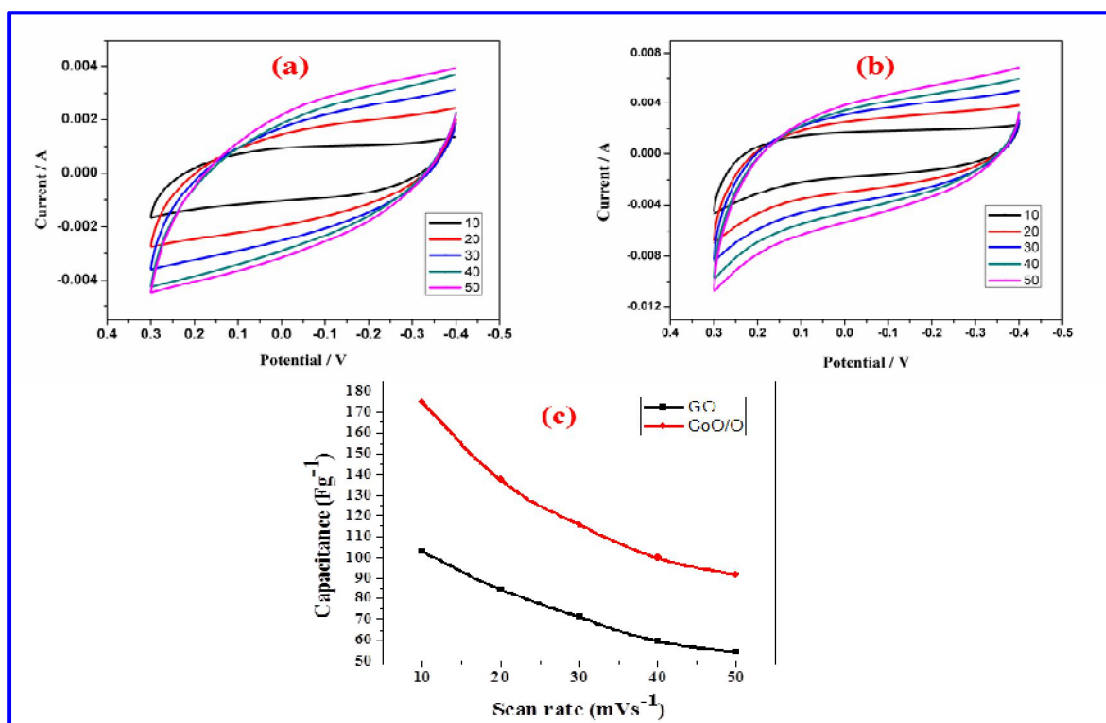


Fig. 7: (a) CV curves of GO at different scan rate. (b) CV curve of rGO-CoO nanocomposite at different scan rate. (c) Specific capacitance of GO and rGO-CoO at various scan rate.

The elemental analysis data clearly indicates that graphene is coordinate with the oxygen atom. In order to verify the presence of Co in the doped graphene oxide samples, the EDS analysis was performed. EDS profile of graphene oxide $C_{0.56}O_{0.44}$ is in figure 6a and graphene oxide-Cobalt oxide

nanocomposite $C_{0.14}Co_{0.36}O_{0.42}$ is prescribed in figure 6b. It clearly revealed that the product is composed of C, O and Co elements.

The electrochemical performance of rGO-CoO nanocomposite is examined and those of

graphene oxide are studied for comparisons. The cyclic voltammetry (CV) curves for graphene oxide and reduced graphene oxide-cobalt nanocomposite is nearly rectangular in shape inferring good charge circulation within the electrodes and the electrical double layer capacitance, as shown in figure 7a and 7b. It indicates redox peaks (~0.3 V oxidation peak and -0.4 V reduction peak) and that provide pseudo capacitance reactions.

The specific capacitance of the electrode can be calculated using the following equation.

$$\text{Specific capacitance, } C = I/(dV/dt)m$$

Where,

$$I = \text{current of the both oxidation and reduction peaks} \\ (I = (I_a - I_c) / 2),$$

dV/dt = applied scan rate,

m = weight of the sample coated on the surface of the electrode.

The specific capacitance of Graphene oxide and rGO-CoO nanocomposite was shown fig. 7c and the calculated values were shown in Table.1. The prepared Co/GO showed enhanced capacitance of 175 Fg^{-1} at 10 mVs^{-1} and 91.8 Fg^{-1} at high scan rate of 50 mVs^{-1} .

This increase in capacitance for composite electrode can be related to the synergy effect by rGO-CoO. GO can act as an electric double layer capacitance for fast charging and discharging and also as a stable layer structured block to restrict the volume change of CoO. Also the CoO doped with GO provided electrochemical reaction sites and ion intercalation spots which were accessible to electrolytes effective (Li *et al.* 2013). When compared with graphene oxide, rGO-CoO composite is found to report enhanced electrical conductivity and improved electrochemical performance in terms of cyclic ability.

Table 1. Specific capacitance of GO and rGO-Co as a function of rates

| | 10 mVs^{-1} | 20 mVs^{-1} | 30 mVs^{-1} | 40 mVs^{-1} | 50 mVs^{-1} |
|--|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Capacitance GO (Fg^{-1}) | 103 | 84.5 | 71 | 59.5 | 54.2 |
| Capacitance rGO-CoO (Fg^{-1}) | 175 | 137.5 | 115.67 | 99.75 | 91.8 |

4. CONCLUSION

The rGO/CoO nanocomposite with an average diameter of 10 nm was successfully prepared by low temperature co-precipitation route within as minimum as 6 h reaction time and as low as 85°C . The final product was annealed at 500°C . The as prepared nanocomposite was characterized using different tools like, XRD, IR, XPS, TEM and SEM. The specific capacitance of rGO-CoO composites was 175 Fg^{-1} at 10 mVs^{-1} compared to 103 Fg^{-1} of GO. The rGO/CoO nanocomposite show a favorable electrochemical capacitor property, which is attributed to its high electrical conductance and excellent cyclic ability.

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REFERENCES

- Ashok Kumar, N., Choi, H., Ran Shin, Y., Chang, D., Dai, L. and Baek, J., Polyaniline-Grafted reduced graphene oxide for efficient electrochemical super capacitors. *ACS. Nano.* 6(2), 1715-1723(2012).
doi:10.1021/nn204688c
- Bao, C., Song, L., Charles, W., Yuan, B., Guo, Y., Hu, Y. and Gong, X., Graphite oxide, graphene, and metal-loaded graphene for fire safety applications of polystyrene, *J. Matter. Chem.*, 22(17), 16399-16406(2012).
doi:10.1039/c2jm32500d
- Chen, S., Zhu, J., Han, Q., Zheng, Z., Yang, Y. and Wang, X., Shape-Controlled synthesis of one-dimensional MnO_2 via a facile quick-precipitation procedure and its electrochemical properties, *Crystal Growth & Design.*, 9(5), 4356-4361(2009).
doi:10.1021/cg900223f
- Dong, X., Xu, H., Wang, X., Huang, Y., Chan-Park, B., Zhang, H., Wang, L., Huang, W. and Chen, P., 3D Graphene-Cobalt oxide electrode for high performance super capacitor and enzymeless glucose detection, *ACS Nano.*, 6(4), 3206-3213(2012).
doi:10.1021/nn300097q
- Elzatahry, A., Abdullah, A., Salah El-Din, T., Al-Enizi, A., Maarouf, A., Galal, A., Hassan, H., El-Ads, E Al-Theyab, S. and Al-Ghamdi, A., Nanocomposite graphene-based materials for fuel cell applications, *Int. J. Electrochem. Sci.*, 7(13), 3115-3126(2012).

- Fan, S., Zhang, Y., Ma, X., Yan, E., Liu, X., Li, S., Liang, W. and Zhai, X., Deposition of Nanocrystal Co_3O_4 on grapheme nano sheets as anode material for lithium ion batteries, *Int. J. Electrochem. Sci.*, 8(5), 10498-10505(2013).
- Gao, L., Yue, W., Tao, S. and Fan, L., Novel strategy for preparation of graphene-Pd, Pt Composite, and its enhanced electrocatalytic activity for alcohol oxidation, *Langmuir*, 29(8), 957-964(2013).
[doi:10.1021/la303663x](https://doi.org/10.1021/la303663x)
- Gao, W., Majumder, M., Alemany, B., Narayanan, N., Ibarra, A., Pradhan, K. and Ajayan, M., Engineered graphite oxide materials for application in water purification. *ACS Appl. Mater. Interfaces.*, 3, 1821-1826(2011).
[doi:10.1021/am200300u](https://doi.org/10.1021/am200300u)
- Hu, H., Zhao, Z., Zhou, Q., Gogotsi, Y. and Qiu, The role of microwave absorption on formation of graphene from graphite oxide, *J. Carbon.*, 50(9), 3267-3273(2012).
[doi:10.1016/j.carbon.2011.12.005](https://doi.org/10.1016/j.carbon.2011.12.005)
- Hummers, W. S., Offerman, R. E., Preparation of graphite oxide., *J. Am. Chem. Soc.* 80(5), 1339-1339(1958).
[doi:10.1021/ja01539a017](https://doi.org/10.1021/ja01539a017)
- Jiang, Y., Zhang, Q., Li, F., Niu, L., Glucose oxidase and graphene bio-nanocomposite bridged by ionic liquid unit for glucose bio-sensing application, *Sensors and Actuators*, 161(1), 728-733(2012).
[doi:10.1016/j.snb.2011.11.023](https://doi.org/10.1016/j.snb.2011.11.023)
- Lee, S., Mattevi, C., Chhowalla, M. and Sankaran, R., Plasma-assisted reduction of graphene oxide at low temperature and atmospheric pressure for flexible conductor applications, *J. Phys. Chem. Lett.*, 3(6), 772-777(2012).
[doi:10.1021/jz300080p](https://doi.org/10.1021/jz300080p)
- Li, D., Shi, D., Chen, Z., Liu, H. and Jia, D., Enhanced rate performance of cobalt oxide/nitrogen doped graphene composite for lithium ion batteries, *RSC Advances*, 3(15), 5003-5008(2013).
[doi:10.1039/c3ra22765k](https://doi.org/10.1039/c3ra22765k)
- Lian, P., Zhu, X., Liang, S., Li, Z., Yang, W. and Wang, H., Large reversible capacity of high quality graphene sheets as an anode material for lithium-ion batteries, *Electro. Chemica. Acta.*, 55(8), 3909-3914(2010).
[doi:10.1016/j.electacta.2010.02.025](https://doi.org/10.1016/j.electacta.2010.02.025)
- Park, S., Park, S. and Kim, S., Preparation and capacitance behaviors of cobalt oxide/graphene composites, *Carbon Lett.*, 13(2), 130-132(2012).
[doi:10.5714/CL.2012.13.2.130](https://doi.org/10.5714/CL.2012.13.2.130)
- Wang, L., Li, J., Mao, C., Zhang, L., Zhao, L., Jiang, Q., Facile preparation of a cobalt hybrid/grapheme nano composite by in situ chemical reduction: high lithium storage capacity and highly efficient removal of congo red, *Dalton Trans.*, 42(4), 8070-8077(2013).
[doi:10.1039/c3dt50333j](https://doi.org/10.1039/c3dt50333j)
- Wood, C., Ogitsu, T., Otani, M. and Biener, J., First principle inspired design strategies for graphene based super capacitor electrodes, *J. Phys. Chem. C.*, 118(1), 4-15(2014).
[doi:10.1021/jp4044013](https://doi.org/10.1021/jp4044013)
- Wu, Z., Zhou, G., Yin, L., Ren, W., Li, F. and Cheng, H., Graphene/metal oxide composite electrode materials for energy storage, *Nano Energy.*, 1(1), 107-131(2012).
[doi:10.1016/j.nanoen.2011.11.001](https://doi.org/10.1016/j.nanoen.2011.11.001)
- Xu, G., Wang, N., Wei, J., Lv, L., Zhang, J., Chen, Z. and Xu, Q., Preparation of Graphene oxide/polyaniline nanocomposite with assistance of super critical carbon dioxide for super capacitor electrodes, *Ind. Eng. Chem. Res.*, 51(4), 14390-14398(2012).
[doi:10.1021/ie301734f](https://doi.org/10.1021/ie301734f)
- Yan, J., Wei, T., Qiao, W., Shao, B., Zhao, Q., Zhang, L. and Fan, Z., Rapid microwave-assisted synthesis of graphene nanosheet/ Co_3O_4 composite for super capacitors, *Electro. Chemica. Acta.*, 55(7), 6973-6978(2010).
[doi:10.1016/j.electacta.2010.06.081](https://doi.org/10.1016/j.electacta.2010.06.081)
- Yao, Y., Xu, C., Qin, J., Wei, F., Rao, M. and Wang, S., Large reversible capacity of high quality graphene sheets as an anode material for lithium-ion batteries, *Ind. Eng. Chem. Res.*, 52(13), 17341-17350(2013).
[doi:10.1021/ie401690h](https://doi.org/10.1021/ie401690h)
- Zhang, L., Huang, Y., Zhang, Y., Ma, Y. and Chen, Y., Sol-Gel Autocombustion Synthesis of Graphene/Cobalt magnetic nanocomposites, *J. Nanosci. Nanotechnol.*, 13(2), 1129-1131(2013).
[doi:10.1166/jnn.2013.6000](https://doi.org/10.1166/jnn.2013.6000)
- Zheng, Y., Li, P., Li, H., Chen, S., Controllable growth of cobalt oxide nanoparticles on reduced graphene oxide and its applications for highly sensitive glucose sensor. *Int. J. Electrochem. Sci.*, 9(7), 7369-7381(2014).
- Zhu, J., Sharma, Y., Zeng, Z., Zhang, X., Madhavi, S., Mhaisalkar, S., Zhang, H., Hng, H. and Yan, Q., Cobalt oxide nanowall arrays on reduced graphene oxide sheets with controlled phase, grain size, and porosity for Li-Ion battery electrodes, *J. Phys. Chem. C.*, 115(5), 8400-8406(2011).
[doi:10.1021/jp2002113](https://doi.org/10.1021/jp2002113)